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Jim Fish provided me several documents concerning ground water contamination with sulfolane that originated at the North Pole Refinery, North Pole, Alaska.

- 1) A study Plan Jim Fish put together to identify specific degradation questions and how they will be answered
- 2) A power point file that outlines potential degradation pathways found in the literature and possible intermediate products that may be formed
- 3) Bench-scale testing of sulfolane degradation conducted by Barr Engineering
- 4) On-site pilot air-sparge studies conducted by Barr Engineering
- 5) A summary of potential aerobic degradation pathways (abiotic and biological) prepared by Dr. Lisa Gieg (Uni. of Calgary)
- 6) Results of CSIA and a PLFA-SIP experiment on-site at the Refinery presented by Arcadis (these results have not been submitted to ADEC yet).
- 7) A follow up CSIA and a PLFA-SIP experiment on-site at the Refinery and at locations down gradient of the spill location.

Mr. Fish identified his goal as being "...able to answer how sulfolane is being degraded both on-site and off-site, determine if MNA is sufficiently protective and how best to evaluate MNA. A related goal would be understand how sulfolane is removed in Point-of-Entry GAC water filtration systems in private residences (we suspect biodegradation). It is likely that MNA will be proposed as cleanup approach to groundwater off-site of the refinery, while an air-sparge curtain has recently been proposed as an on-site remedial action to stop off-site sulfolane migration."

How is sulfolane being degraded?

When oxygen is added to ground water at the air sparging demonstration, pre-existing concentrations of sulfolane were brought below the detection limit with a few weeks after the concentrations of oxygen exceed 2 to 3 mg/L [Table 4, pages 28-35 of 54, in Technical Memorandum Air Sparge Pilot Test – Results Evaluation Revised January 18, 2013, Flint Hills Resources Alaska, LLC, North Pole Refinery]. The simplest explanation for the disappearance of sulfolane in the air sparging demonstration is aerobic biodegradation.

The ground water that contains detectable sulfolane has low concentrations of dissolved oxygen (on the order of 0.2 mg/L) and high concentrations of Iron(II). Iron(II) is rapidly oxidized by dissolved oxygen. Iron(II) and dissolved oxygen cannot occur together at detectable concentrations in ground water. It is likely that the low concentrations of oxygen are either artifacts of oxygen contamination from the atmosphere during sampling, or represent oxygenated flowpaths in the aquifer that contribute relatively little water to the total flow to the monitoring well.

As an example, Table 17 on page 94 of 148 of the report titled: Flint Hills Resources Alaska, LLC, Third Quarter 2012 Groundwater Monitoring Report North Pole Refinery, North Pole, Alaska, DEC File Number: 100.38.090, October 31, 2012, indicates the concentration of oxygen in water produced from the well was 0.15 mg/L while the concentration of Iron(II) was 11.2 mg/L.

The report indicates that sulfolane is degraded under aerobic conditions in ground water at the site. If oxygen were available in the aquifer for sulfolane degradation, it is reasonable to presume that the sulfolane would already be degraded. The sulfolane that remains in the aquifer must exist in oxygen free water. Any biological or abiotic mechanisms for sulfolane degradation under ambient (natural or MNA) conditions must function under anaerobic conditions.

How best to evaluate MNA.

In an attempt to recognize transformation reactions for sulfolane contamination in ground water, the evaluated isotopic fractionation of ^{14}C in sulfolane with distance down gradient of the spill site. Arcadis and their associates did a high quality study of the distribution of values of $\delta^{13}\text{C}$ in sulfolane in the contaminated ground water. Flint Hills Resources Alaska, LLC, Bio-Studies Summary Report, North Pole Refinery, February 2013. They were able to show that the values for $\delta^{13}\text{C}$ in sulfolane in wells MW-182 and MW-161 were different from values in the on-site wells at 95% confidence. However, the fractionation is very modest. The range of values on-site was -30.6‰ to -29.4‰. The highest value recorded in the down gradient wells was -27.4‰.

If the anaerobic biodegradation of sulfolane at the sites goes through an initial reduction of sulfolane to thiolane, no chemical bond to a carbon atom is involved, and there is no reason to expect the carbon to fractionate. As a result, the isotopic enrichment factor (ϵ) would have a small absolute value, and the predicted extent of degradation from the small change in $\delta^{13}\text{C}$ in sulfolane would be large. A careful laboratory microcosm study of the anaerobic degradation of sulfolane in sediment from this site would allow an estimate of the extent of degradation from the extent of fractionation.

As is discussed later, the rate constants for degradation in the down gradient portions of the plume will be no more than 0.2 to 0.9 per year. To get good kinetics and a reasonable comparison of fractionation,

it is desirable to see an order of magnitude reduction in concentration in the microcosm study used to extract the rate constants and fractionation factors. If the rate in the microcosm is the rate in the field, the incubation period would need to extend for three years or more.

If thiolane is the major degradation product of sulfolane, then fractionation of the sulfur atom or oxygen atom should be large. Doing CSIA for isotopes of sulfur and oxygen may be something to consider, but if you do consider CSIA for oxygen, consult an expert and see if the oxygen would be expected to exchange with water. If it does, then CSIA of oxygen has no value.

As is suggested in the review done by the University of Alaska on possible mechanisms of degradation, there may be more than one mechanism for anaerobic biodegradation of sulfolane, and different mechanisms may have different values for the isotopic enrichment factor (ϵ). The thermodynamic feasibility of anaerobic biodegradation can be sensitive to the concentration of the substrate. You want the dominant mechanism in the microcosm study to be the dominant mechanism at field scale. I would restrict the concentrations of sulfolane in the microcosm study to concentrations actually seen at field scale. Higher concentrations may facilitate a different mechanism of degradation.

In an attempt to determine if contaminated ground water contains bacteria that can degrade sulfolane, they conducted stable isotope probing (SIP). The basic idea behind SIP is to provide ^{13}C labeled sulfolane to the natural bacteria, and see if the ^{13}C label shows up in degradation products such as dissolved inorganic carbon or methane. The approach assumes that the entire amount of ^{13}C label comes from the substrate being studied. This is never entirely the case. It is impossible to prepare any organic compound in a form that is absolutely pure. If material used to bait the BioSep beads contains ^{13}C label that is associated with some other compound, then biodegradation of the other compound or compounds would be attributed to sulfolane. The only control for this false signal is to compare the quantity of impurity and the ^{13}C label in the impurity to estimate the total amount of ^{13}C label in the impurity that is presented to the bacteria, and then compare the total amount of label transferred to degradation products.

Consult Table 12 on page 19 of 225 in Appendix G of Flint Hills Resources Alaska, LLC Bio-Studies Summary Report, North Pole Refinery, February 2013. The “no amendment” treatments are relevant to degradation under ambient conditions in the ground water. During the period of incubation, they could document degradation of 0.5%, 1.6%, 0.7% and 0.8% of the sulfolane supplied, based on accumulation of ^{13}C label in inorganic carbon.

Consult page 16 of 225. They state: *The $^{13}\text{C}_4$ -sulfolane 94% chemical purity with 1.18% water & 3.93% unlabeled impurity with 99.51% ^{13}C enrichment.* I do not understand what they mean by the statement. Are they saying that all the impurities that they can separate and measure are not labeled? There is 0.89% missing. It does raise the possibility there is more than enough impurity to provide the entire amount of ^{13}C label collected in the DIC in the probes placed in wells MW-142, MW-148A, and MW-30. Arcadis should require that Microseeps provide the team a copy of their certificate of analysis of the $^{13}\text{C}_4$ -sulfolane. The real question is the isotopic purity of the preparation. How much ^{13}C is associated with other organic compounds that might be biodegradable? If that information is not available from the certificate of analysis, then the $^{13}\text{C}_4$ -sulfolane should be analyzed to determine the isotopic purity.

Another line of evidence for biodegradation is the distribution of concentrations of sulfolane in the ground water. I estimated the contribution of degradation by comparing the discharge (sometimes called flux) across four transects.

Consult Figure 14 on page 128 of 148 of the report titled: Flint Hills Resources Alaska, LLC, Third Quarter 2012 Groundwater Monitoring Report North Pole Refinery, North Pole, Alaska, DEC File Number: 100.38.090, October 31, 2012. The first transect is the vertical profiling transect. The second is drawn through the center of the cluster of wells in the neighborhood some 0.6 miles down gradient of the vertical profile transect. The third is a transect from MW-161 to MW-164 that is some 2 miles down gradient of the vertical profile transect. This represents a region of high concentrations far down gradient of the source. The fourth is a transect through wells MW194 and MW-167, some 3 miles down gradient of the vapor profiling transect.

We draw smooth plume outlines, but that is a graphical conceptualization of our ignorance. Comparing attenuation in concentrations from one well to another is prone to error because we have no guarantee that the two wells lie along a flow path. Comparing the discharge across transects can reduce but certainly does not eliminate that source of error.

Monitoring well MW-182 is approximately three miles (151,167 feet) down gradient of the most contaminated well on the site. The monitoring record for sulfolane begins in the spring of 2006. If the contamination took six years to reach MW-182, the seepage velocity would be at least 7 feet per day (column **G** of tab **Rate Constant Calculations**). The contamination has not reached MW-311-46, which is more than four miles down gradient. The seepage velocity would be no larger than 10 feet per day (column **G** of tab **Rate Constant Calculations**). I am aware of a few sites where the seepage velocity was this high. Seepage velocities of 7 and 10 feet per day would be equivalent to 800 and 1100 meters per year. Compare the chart below.

Seepage Velocity of Chlorinated Solvent Plumes in USA

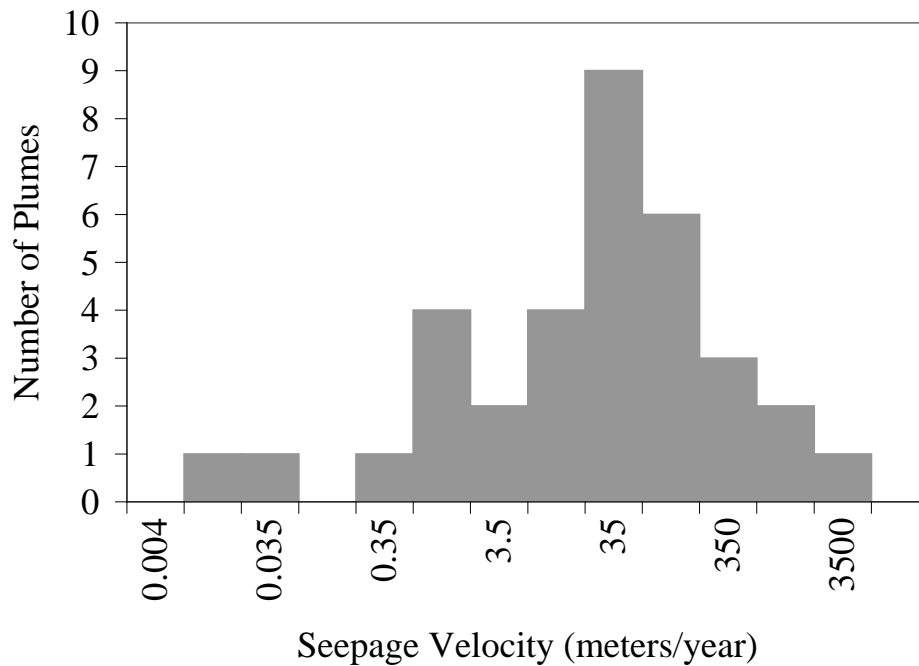


Table 1 uses the distance along the flow path and the boundaries on the seepage velocity to estimate a high and low travel time from the vapor profile transect to the down gradient transects. You will have to determine if this range of seepage velocities is plausible in the more transmissive portions of the contaminated aquifer. The calculations assume the plume has been in the ground water for only six years. If you have better information on the date of the release, you can put that information into column **G** of tab **Rate Constant Calculations**, and refine the estimates of seepage velocity.

Table 1. Estimates of seepage velocities and travel times to wells or transects down gradient of the vertical profile (VP) transects.

Location	Distance from VP Transect	Time since Release	Seepage Velocity	High Estimate Travel Time	Low Estimate Travel Time
	(feet)	Years	Feet per Day	Years	Years
MW-311-46	22667	6	10.3	9.0	6.0
3 miles down gradient of VP transect	15167	6	6.9	6.0	4.0
2 miles down gradient of VP transect	10333			4.1	2.7
0.63 miles down gradient of VP transect	3333			1.3	0.9

I multiplied the width of the transect by the depth of contaminated water to estimate a contaminated cross section perpendicular to ground water flow. I assume the seepage velocity was 7 feet (2.1 meters) per day and that the effective porosity was 0.3. Under these conditions, the darcy velocity is 0.64 meters per day. I multiplied the cross section by the darcy velocity to estimate the discharge of water. I multiplied the average concentration of sulfolane (or an assumed concentration of sulfolane) by the discharge of water to estimate the discharge of sulfolane across each transect. The results are in the table below.

The sulfolane plume leaving the facility seems to be constrained laterally between monitoring wells MW-306 and MW-301. The wells are separated by a lateral distance perpendicular to ground water flow of approximately 1633 feet and the plume is constrained by 50 vertical feet [Figure 17 of Flint Hills Resources Alaska, LLC, Third Quarter 2012 Groundwater Monitoring Report, North Pole Refinery, North Pole, Alaska, October 31, 2012]. The cross section of the plume is 81,633 square feet or 7584 square meters. The average concentration in wells MW-302, 303, 304, and 305 is 61 µg/L, or 0.000061 g/m³. If the porosity is 0.3 and the seepage velocity is 7 feet or 2.1 meters per day, the discharge of the plume across the transect between MW-306 and MW-301 is near 4854 cubic meters of water per day and 297 grams sulfolane per day.

Compare Table 2 of this document. The current discharge of sulfolane at the vertical profile transect at the refinery boundary is roughly (very roughly) an order of magnitude lower than at a location two miles down gradient. It is roughly half of the discharge across transects that are 0.6 and 3 miles down gradient of the refinery boundary. This pattern is to be expected when the rate of natural attenuation of the source plus the rate of active remediation of the source is greater than the rate of natural attenuation along the flow path in ground water.

Table 2. Discharge of water and sulfolane across transects perpendicular

Transect	Area	Water Discharge	Sulfolane Discharge
	square meters	cubic meters per day	grams per day
Vertical Profiling transect	7584	4854	297
0.6 miles down gradient of VP transect	8516	5451	640
2 miles down gradient of VP transect	27871	17840	2776
3 miles down gradient of VP transect	28800	18434	542

To estimate the rate of attenuation it will be necessary to compare the current discharge across the down gradient transects to plausible maximum values for the discharge across the vertical profile transect. What if the average concentration in the transect leaving the refinery was the maximum concentration sampled in the transect (284 µg/L)? Compare Table 3 of this document. The discharge of sulfolane at the refinery boundary would be 1442 grams sulfolane per day, which is roughly comparable to the discharge two miles down gradient. What if the average concentration in the transect leaving the refinery was the maximum concentration sampled in the source area in the refinery (4940 µg/L)? The discharge of sulfolane at the refinery boundary would be 23980 grams sulfolane per day, which is roughly an order of magnitude greater than the discharge two miles down gradient.

Table 3. Comparison of the actual discharge of sulfolane across the vertical profile transect to two estimates of the hypothetical maximum discharge

Transect	Area	Water Discharge	Sulfolane Discharge
	square meters	cubic meters per day	grams per day
Vertical Profiling transect	7584	4854	297
Vertical Profiling transect assume 284 µg/L	7584	4854	1442
Vertical Profiling transect assume 4940 µg/L	7584	4854	23980

Consult Table 4. These two assumed values for the concentration of sulfolane crossing the vertical profile transect were used to estimate reasonable upper boundaries on the rate constant for anaerobic biodegradation of sulfolane in the contaminated plume.

Table 4. Estimates of the rate of degradation between the transects.

Location	High Estimate Travel Time	Low Estimate Travel Time	Initial Sulfolane Discharge	Final Sulfolane Discharge	High Estimate Rate Constant	Low Estimate Rate Constant
	Years	Years	gm per day	gm per day	per Year	per Year
3 miles down gradient	6.0	4.0	23980	542	0.9	0.6
3 miles down gradient	6.0	4.0	1442	542	0.2	0.2
2 miles down gradient	4.1	2.7	23980	2776	0.8	0.5
2 miles down gradient	4.1	2.7	1442	2776		
0.63 miles down gradient	1.3	0.9	23980	640	4.1	2.7
0.63 miles down gradient	1.3	0.9	1442	640	0.9	0.6

Even with these extremely generous assumptions about the discharge of sulfolane leaving the facility, the rate constant for sulfolane degradation between the refinery boundary and the two transects that are two and three miles down gradient are in the range of 0.2 to 0.9 per year. The range of rate constants to the transect in the neighborhood 0.6 miles down gradient are higher. They are in the range often seen for BTEX compounds. It is likely that the rate of anaerobic sulfolane degradation in the contaminated ground water is slow, if it occurs at all. However rates of this magnitude have proven to be useful for MNA at other sites.

How to determine if MNA is sufficiently protective.

The only way to determine if MNA is sufficiently protective of ground water quality is to select a clean-up goal (you have one, 14 µg/L) and a date at which that date will be attained, or alternatively a boundary beyond which the plume cannot pass at concentrations above the goal. If you will identify which goal applies for this site, I can make some further projections. It would be helpful to have time trend data for critical wells such as MW-161, MW-164, MW-182, MW-194, MW-392-66, and MW-329-15.

How is sulfolane removed in Point-of-Entry GAC water filtration systems in private residences?

I have no expertise in this area. The report provided by Arcadis raises the possibility of aerobic biodegradation of sulfolane sorbed to the activated carbon. This is a reasonable possibility, but I would feel more comfortable that this might occur if the concentration of dissolved oxygen in the water leaving the GAC water filtration system was in the range of 3 to 5 mg/L or higher.